AD-A172 096 SURFACE FUNCTIONALIZED POLYETHYLENE FILM(U) HARVARD UNIV CAMBRIDGE MASS DEPT OF CHEMISTRY G M WHITESIDES JUN 86 4 N00014-83-K-0142 1/1

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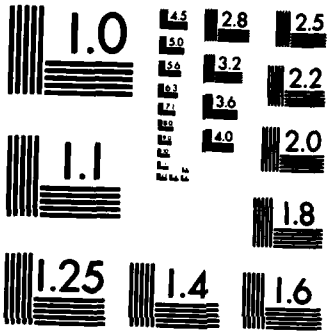

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This project has:

1) Developed practical methods for oxidizing the surface of low-density polyethylene film and introducing reactive organic functionality into this oxidized surface layer.

2) Explored new techniques for analyzing the surfaces of organic polymeric solids. "Contact angle titration"--the study of the contact angle of water on organic solids as a function of pH--has proved particularly useful and extremely surface sensitive.

3) Characterized a series of new phenomena occurring in thin organic surface layers, including thermal reconstruction of the surface (a process during which functional groups in the surface migrate into the deeper parts of the polymer).

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4) Examined the basic physical organic chemistry of wetting of organic solids.

5) Applied the information from these studies to the synthesis of new interface-modifying agents, especially for adhesion promotion.

OFFICE OF NAVAL RESEARCH

FINAL TECHNICAL REPORT

for

Contract N-00014-83-K-0142

Task No. NR 531-840

Surface Functionalized Polyethylene Film

George M. Whitesides

Harvard University

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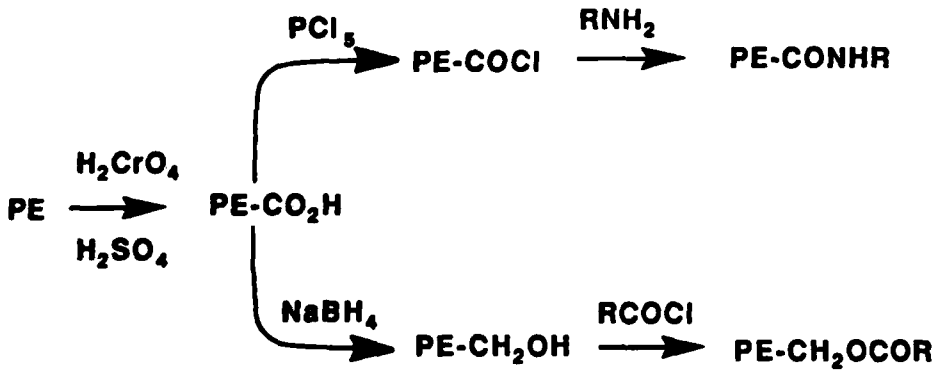
This work has:

1) Developed new preparative techniques for modifying the interfacial properties (especially the wettability) of polyethylene. Polyethylene was chosen as a representative, widely available organic polymer. It is particularly attractive for use in studies of the sort pursued here because it has no background organic functionality, and hence is easy to use as a model system in studies concerned primarily with the influence of organic functional groups on polymer interface properties. It is also non-polar, and the bulk polymer is thus easily distinguished from polar surface functional groups.

We have devised a number of successful techniques capable of introducing a wide range of substituents into the polymer interface. These methods all start with oxidation of polyethylene to a material containing carboxylic acid groups in its surface (called here PE-CO_2H, "polyethylene carboxylic acid"). This method of oxidation was selected because it is relatively clean: after oxidation, the only functional groups present are carboxylic acid and ketone/aldehyde moieties. The procedures used thereafter follow standard techniques of organic synthesis to attach functional groups R of interest (eq 1).



2) Demonstrated the particular utility of contact angle measurements as a method of characterizing organic functionality present in low interfacial free energy solids. Contact angle measurements have the characteristic that they are easy to carry out, using inexpensive apparatus. Analytical methods based on contact angle measurements are thus, in principle, widely usable in organic interfacial chemistry. Contact angle measurement has been widely neglected in the last years, relative to vacuum physics, because of the difficulties in interpreting certain aspects of the measurements in molecular terms. We have used it extensively both for its simplicity, and particularly because of its demonstrated very high sensitivity to groups in the interphase. It appears, in our experience, to be much more "surface-sensitive" than are techniques such as photoelectron spectroscopy. Further, it is applicable to the study and characterization of solid-liquid interfaces.

A technique that we call contact angle titration--examination of the pH dependence of contact angle--has proved especially useful in characterizing surfaces containing acidic and basic functional groups. Since many of our schemes for polymer interface modification are based upon such reactive groups, contact angle titration has formed the single most useful technique in our experiments.

The fundamental physical chemistry underlying the phenomenon of wetting on the types of interfaces encountered in this work remains unclear. The measurements we make are subject to pronounced hysteresis. Hysteresis is commonly attributed to heterogeneity on the surface at the scale of microns. Although the surfaces produced in this work are certainly rough on the scale, it is not obvious that they are heterogeneous with this dimensionality (although they are certainly heterogeneous at the scale of 5-100 Å). We

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presently believe the heterogeneity is due to reactive wetting--that is, a phenomenon analogous to the more widely studied "dry" spreading. That is, wetting is not a reflection of equilibrium thermodynamics of the system, but rather of a complex and still incompletely understood balance between kinetic and thermodynamic factors. We are still examining this phenomenon both theoretically and experimentally.

3) Development fluorescence probes based on the Dansyl group as an aid to characterizing functionalized polymer interfaces.

4) Initiated studies of the relations between molecular-level interface properties and macroscopic materials properties of functionalized polymer films. The long-range objective of our work is to make rational, science-based correlations between the atomic-level structure of interfaces and their macroscopic physical properties (e.g., wettability, barrier film characteristics, adhesive strength). Much of our work to date has involved studies of wetting, and we are beginning to understand the connections between the polarity of functional groups at an interface and the wettability of that interface. This type of correlation is, of course, of both basic and applied interest (the latter, for example, in controlling the spreading of liquid matrix polymer in the assembly of fiber-reinforced composites). We have also started on more complex materials problems such as adhesion. Initial studies have established that the strength of adhesion to functionalized polyethylene film in certain test systems correlates well with the presence of polar functional groups in the contact-angle interphase.

We have applied our knowledge of relations between adhesive strength and molecular properties to the design of an adhesion promoter between polished gold and polyethylene. This adhesion promoter is a designed surface active agent having the structure $HS(CH_2)_{11}CH{=}CH_2$. This material was predicted

(successfully) to be capable of linking gold and plasma-deposited polyethylene covalently, and thus to dramatically promote adhesion of gold and polyethylene.

List of Technical Reports

Technical Report No. 85-1
Acid Base Behavior of Carboxylic Acid Groups Covalently Attached at the Surface of Polyethylene: The Usefulness of Contact Angle in Following the Ionization of Surface Functionality
by Stephen Randall Holmes-Farley, Robert H. Reamey, Thomas J. McCarthy, John Deutch, and George M. Whitesides
Document Type: Preprint
August 1985

Technical Report No. 85-2
Fluorescence Properties of Dansyl Groups Covalently Bonded to the Surface of Oxidatively Functionalized Low-Density Polyethylene Film
by Stephen Randall Holmes-Farley and George M. Whitesides
Document Type: Preprint
December 1985

Technical Report No. 85-3
Improved Adhesion of Thin Conformal Films to Metal Surfaces
by Kevin P. Stewart and George M. Whitesides
Herman P. Godfried and Isaac F. Silvera
Document Type: Preprint
May 1986

List of Publications

"Acid-Base Behavior of Carboxylic Acid Groups Covalently Attached at the SUrface of Polyethylene: The Usefulness of Contact Angle in Following the Ionization of Surface Functionality" Holmes-Farley, S.R.; Reamey, R.H.; McCarthy, T.J.; Deutch, J.; Whitesides, G.M. Langmuir **1985**, 1, 725-740.

"Fluorescence Properties of Dansyl Groups Covalently Bonded to the Surface of Oxidatively Functionalized Low-Density Polyethylene Film" Holmes-Farley, S.R.; Whitesides, G.M. Langmuir **1986**, 2, 266-281.

"Improved Adhesion of Thin Conformal Films to Metal Surfaces" Stewart, K.R.; Whitesides, G.M.; Godfried, H.P.; Silvera, I.F. Rev. Sci. Instr. **1986**, in press.

APPENDIX

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